

LASER-INDUCED FORMATION OF EXTENDED MODIFIED REGIONS IN FOAM GLASS IMPREGNATED WITH SILVER SALTS

M. M. Sergeev^{1,2} and G. K. Kostyuk¹

Translated from *Steklo i Keramika*, No. 4, pp. 7 – 13, April, 2014.

A method of writing extended modified regions with complex structure, which can act as waveguide microstructures in the interior of porous glass plates impregnated by solutions of silver salts, by means of 1.07 μm continuous-wave ytterbium fiber laser is examined. The results of studies of extended modified regions by optical methods are presented. Similar microstructures in the interior of glass can easily become base elements of fiber-optic systems for different applications.

Key words: laser-induced formation, local optical modification, photochromic porous glass.

The rapid development of fiber and integrated optics requires devising and producing increasingly newer multifunctional devices with complex architecture which are capable of processing, transforming and controlling optical signals in a wide spectral range [1]. Such devices are already being widely used in diagnostics, control and analysis of different physical processes occurring in gases, liquids and solids and at the boundaries of different media. The application of such devices is based on measuring the characteristics and parameters of a process, such as the temperature, pressure and chemical composition of substances participating in a process and many others [2].

The expansion of the range of measurable parameters by means of such devices while preserving and even decreasing their size requires an even more complicated device architecture, a reduction of the size of individual elements and higher placement density of the elements per unit volume of the material used as the base for device production.

Three-dimensional writing of the elements in the interior of the material is now proceeding in two directions. In one direction the production of the complicated device architecture is based on the use of a technology for depositing and treating film coatings on semiconductors, first and foremost, silicon, as the most studied material [3]. The second one is based on the use of different methods of treating glass ceramic materials and glass transparent to visible-range optical signals.

One material suitable for producing devices with complex architecture is a photosensitive glass containing atoms

of Ag, Cu, Fe, Nd and other metals [4]. Mainly laser technologies are used to produce modified regions (MR) of different shapes and sizes, representing the main elements of devices on the surface and in the interior of glass ceramics and glass [5, 6]. Laser technologies are used because they make it possible to control quite accurately the optical characteristics and the size and shape of MR by controlling the parameters of the writing radiation even during the formation of MR. At the present time the radiation from femtosecond lasers and sources with ultrashort pulse duration about 12 fsec and pulse repetition frequency 600 Hz or higher is used in practically all cases to write three-dimensional structures in the interior of optically transparent materials. Working with emitters of this kind complicates the MR formation technology on account of self-focusing and channelization of the radiation when it is focused in the interior of the material. Such processes adversely affect the integrity of MR during writing. Another adverse factor of using radiation with femtosecond pulse duration in MR writing technologies is the high cost of such technologies.

A technology for forming MR in the interior of high-silica porous glass (PG) plates by using continuous wave laser radiation weakly absorbed in PG was recently proposed [7]. The preservation of MR and the stability of their optical characteristics during storage and operation in this technology are obtained by baking plates with MR in a furnace up to the transformation of the PG into high-silica (> 90% SiO_2) quartzoid glass.

It is known that the silica framework of PG, comprising a porous matrix, can be effectively permeated with solutions of different substances [8]. By adjusting the physical and chemical characteristics of solutions of permeating substances it

¹ National Research University of Information Technologies, Mechanics and Optics, St. Petersburg, Russia.

² E-mail: maks-sv-32@yandex.ru.

is possible to achieve partial absorption of laser radiation in the region of the beam waist, as a result of which the temperature increases to 150 – 200°C in the irradiation zone, which is significantly lower than the baking temperature of PG (870°C). When using permeating solutions containing colloidal Ag and Cu particles the temperature in the irradiation zone can reach 750 – 1000°C, which is completely adequate for thermal compaction of the PG framework. Substances which under the laser irradiation can be effectively polarized and oriented relative to the laser radiation, where within the region of beam waist the initial permeating substance can decompose into fractions with new substances as well as stable compounds being formed with physical and chemical characteristics differing from those of the glass matrix, can also be introduced into the permeating solutions. As noted previously, laser writing of MR in the interior of PG plates is an intermediate stage of the technology, after which the PG plates with MR are baked up to the formation of a monolithic quartzoid glass with stable optical properties. For any of the avenues presented above, baking is also mandatory for MR structured under laser irradiation in the interior of a PG plate permeated with a solution of a substance.

In the present work we examine a method of writing extended MR with complex structure in the interior of PG plates, impregnated by a water solution of silver salts, by means of a continuous wave fiber laser. Such a modification, arising in the process of writing, can be viewed as a waveguide structure — a basic element of devices in fiber-optic systems used in different applications. The complex structure of extended MR, revealed in the course of the investigations, opens up new prospects for increasing the functionality of devices by increasing their structural complexity. This will make it possible to use such devices in different areas of science and engineering based on fiber-optic systems.

EXPERIMENTAL PART

Fabrication of Photochromic Porous Glass Matrices

Porous glass plates impregnated with silver salts, so-called photochromic porous glass (PCPG), were used as samples in the experiments. The prospects for using PCPG in laser processing were due to, first and foremost, the relatively small energy input in the formation of MR compared with alternative methods of processing optically transparent materials.

To obtain PCPG plates two-phase alkaline borosilicate glass was treated in two steps: leaching and permeation. Two-phase glasses with the following composition (mass fraction, %) were used as blanks: 7.6 Na₂O, 20.4 B₂O₃, 71.9 SiO₂ and 0.1 Al₂O₃ [9]. For the PG, blanks of two-phase glass were subjected to through permeation in a 3 M solution of HNO₃ (HCl) at 100°C. To remove from the channels in the PG the products of decomposition of the borate phase after leaching the treated PG plates were washed in distilled water and dried at 120°C for 1 h.

At the next treatment step PG with the composition (mass fraction, %) 0.2 Na₂O, 4.3 B₂O₃ and 95.5 SiO₂ [9, 10] was subjected to permeation by the salts AgNO₃ and Cu(NO₃)₂ in two steps: permeation for 24 h at room temperature, after which the samples were dried, followed by permeation at 50°C using the halides KBr, KI and NH₄Cl for 30 min and re-drying. After the permeation step the composition of the porous matrices changed to the following (mass fraction, %): 1.05 Na₂O, 3.7 B₂O₃, 94.11 SiO₂, 1.25 Ag₂O, 0.04 CuO and 0.48 K₂O [11, 12]. Just like the PCPG plates, the PG plates were fabricated in the Laboratory of the Physical Chemistry of Glass at the I. V. Grebenshchikov Institute of Silicate Chemistry at the Russian Academy of Sciences.

Laser Irradiation of PCPG

The next step in the processing of PCPG was laser irradiation, where MR formation occurred in the interior of the PCPG plates. Plane-parallel PCPG plates with thickness 1.5 mm were used as experimental samples. The plates were secured on a coordinate table permitting motion along three coordinates with positioning accuracy $\pm(1 - 2) \mu\text{m}$. The formation of MR in the interior of the PCPG plates occurred under the action of an LK-100-V continuous wave ytterbium fiber laser with wavelength $\lambda = 1.07 \mu\text{m}$, spectral line width $\Delta\lambda = 0.003 \mu\text{m}$, divergence $\theta = 0.26 \text{ mrad}$ and beam size $(1/e - 2)D = 6 \text{ mm}$ at the output and output power instability equal to 1% of the power of the incident radiation.

The size and shape of the MR were determined by the power of the incident radiation, the duration of exposure and size of the beam waist, located in the interior of the PCPG at depth 150 – 200 μm from the surface of the plate and formed during focusing of the radiation with a micro-objective (10 \times , 0.25) with focal length $4.75 \pm 0.25 \text{ mm}$. An extended MR is formed under the action of the radiation focused into the interior of the sample with the PCPG plate moving with the velocity 18 $\mu\text{m/sec}$ relative to the laser beam.

In the course of the experiment the power P_0 of the laser radiation incident on the PCPG plate and the power P_τ passing through it were recorded with a Gentec Solo-2M optical power meter, equipped with a UP19K-110F-H9 optical power detector with accuracy 1% of the measured quantity and equivalent noise power about 1 mW. The measurement of P_0 and P_τ made it possible to determine the absorption power of the PCPG during the formation of the MR. The temperature on the surface of the sample at the center of the region of action was recorded with a Flip Titanium 520 M IR-camera, calibrated before each experiment, with size resolution of the measured region $30 \times 30 \mu\text{m}$ for the temperature interval 300 – 1500°C.

After laser processing the PCPG plates with the MR were investigated with an Axio Imager Carl Zeiss optical microscope in transmitted and linearly polarized light with crossed polarizer and analyzer and magnification $\times 100$. An MSFU-K Yu-30.54.072 microscope spectrophotometer was

used to obtain the transmission spectra of individual parts of the MR in the wavelength range 350 – 900 nm.

An extended MR was written in one scan with incident power 4.4, 5.2, 6.1 and 7.9 W. The transverse size of the extended MR as a function of the incident power varied in the range 38 – 68 μm . The formation of an MR in one scan was not observed at lower laser power. To decrease the transverse size of an extended MR a decision was made to decrease the power of the incident radiation to 3.5 W and to increase the number of scans to 5. These measures made it possible to decrease the size of the transverse section of the structure formed to 8 μm .

After laser irradiation at the final stage of processing the PCPG plates together with MR were baked in a furnace, as a result of which the silica framework of the porous matrix was densified and, in consequence, photochromic quartzoid glass (PCQG) was formed. During baking the plate was heated to temperatures $860 \pm 20^\circ\text{C}$ and held at this temperature for 15 ± 5 min, after which the sample was cooled to room temperature under natural conditions. Baking at the final stage of processing the PCPG was a necessary stage of the MR formation process, because the physical-chemical and optical properties of PCPG, which were determined by its highly extended structure, changed with time.

This method of forming MR made it possible to produce extended MR with an even smaller transverse size to 3 – 5 μm . For this it was necessary to decrease the power of the incident radiation to 2.5 – 3 W and increase the number of scans to 10 or decrease the velocity of the sample to 1 – 2 $\mu\text{m}/\text{sec}$. The reduction of the velocity of the sample increased the time required to produce extended MR. The reduction of the concentration of the particles of colloidal silver in the channels in the PG could also promote a reduction in the transverse size of an extended MR.

DISCUSSION

Extended MR were written in PCPG plates by means of an extended source of laser radiation, which was formed as the sample moved with the velocity v relative to the laser beam waist located in the interior of the plates. In the experiment the modification process was implemented by two methods: longitudinal displacement of the beam waist in the interior of a PCPG plate and transverse displacement of the waist over one or several scans. An MR with complex structure was formed during the writing process. The movement of the beam waist resulted in the formation of a three-dimensional waveguide with a complex structure. Such extended MR consisted of a central part, comprised of a denser structure with no large colloidal particles of silver and an edge layer comprising a region with a porous structure whose channels are filled with colloidal silver particles to a higher degree than the channels of the same layer in the unirradiated region of the PCPG plate.

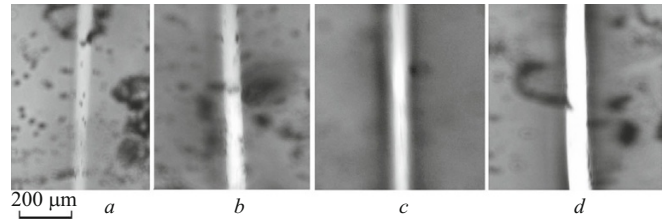


Fig. 1. An extended MR with the focal plane of the microscope in coincidence with the plane of the central part of the MR immediately after irradiation. The scan velocity is 18 – 19 $\mu\text{m}/\text{sec}$; the power of the incident radiation (in W) is 4.4 (a), 5.2 (b), 6.1 (c) and 7.9 (d). The photographs were taken in transmitted light with scale 200 μm .

When the irradiation process reached a stationary state, the temperature at the center of the irradiation zone on the surface of a plate reached about $750 - 850^\circ\text{C}$. The high temperature was due to the low scan velocity of the laser beam as well as the relatively high absorptivity of the PCPG plate, which was determined experimentally to be about 0.22.

In all cases of writing the velocity was 18.5 $\mu\text{m}/\text{sec}$ and the power P_0 of the incident radiation varied from 3.5 to 7.9 W (Fig. 1). Depending on the power of the incident radiation the diameter d_0 of the central part of an extended MR varied from 41 μm for $P_0 = 4.4$ W to 70 μm for $P_0 = 7.9$ W. A change in the power of the incident radiation from 4.4 to 5.2 W resulted in a change in the size of the central region but the contrast between the central part of an extended MR and a PCPG plate remained very small (Fig. 1a and b). In the range $P_0 = 5.2 - 6.1$ W the change in the optical characteristics of the central part of the region, which was manifested in compaction with a very small reduction of its diameter and higher contrast between the central part and the PCPG plate. When the radiation power was subsequently increased from 6.1 to 7.9 W only the diameter of the central part of an extended MR changed; the contrast between the central part and the PCPG plate remained quite high (Fig. 1c and d). The presence of a sharp transition at the boundary of the central part of the region and the plate attested to a large difference in the values of the index of refraction of these regions. At lower incident radiation power, in the case where writing is done in one scan, the formation of a three-dimensional extended MR was not observed.

After laser processing the PCPG plates with MR were baked in a furnace up to the formation of PCQG after which the PCQG with MR was investigated anew. Baking of the plates preserved the extended MR formed in the interior, but the difference of the refractive indices at the boundary between the central part of the region and the PCQG plate, as expected, decreased. The size of the central region also decreased by a factor of 1.4 on average, so that the diameter of the transverse section of an extended MR equal to 70 μm before baking decreased to 50 μm after baking and it decreased from 41 μm to 30 μm . The difference in the refractive indices of the central part of the region and the PCQG was so

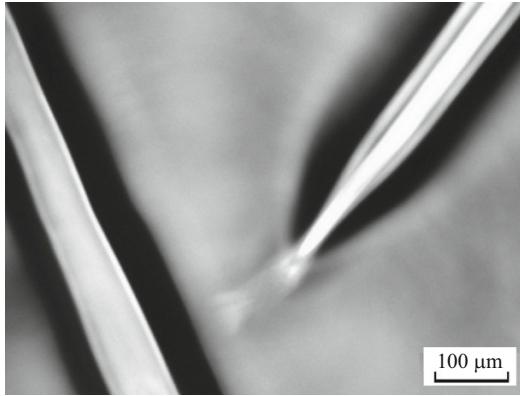


Fig. 2. Two extended MR, which are not butt-jointed with one another, in transmitted light, which were formed with $P_0 = 6.1$ W and $v = 18.5$ mm/sec.

small that an MR in the interior of a plate could be detected only if the focusing plane coincided with the bottom surface of the plate in transmitted light. In this case the transmitted radiation from the illumination system of the microscope was refracted when it passed through the extended MR.

The next step after the optimal regimes for writing extended MR in one scan was writing several extended structures butt-jointed with one another. In this case the process resulting in the formation of the optical modification under the action of the moving source of laser radiation was investigated. In the case where the beam waist moved in the interior of a PCPG plate the successive changes in the optical properties of the waveguide in its central part, viz., a region where the maximum fraction of the laser radiation was concentrated, occurred more rapidly than in the edge part, where the high concentration of silver particles presumably was formed later. This is especially clearly seen where the joint of the extended MR was absent because the irradiation stopped prematurely while the sample was still moving (Fig. 2). For scan rate $18.5 \mu\text{m}/\text{sec}$ and waist diameter about $52.5 \mu\text{m}$ the duration of the action did not exceed 2.84 sec, while the power of the fiber laser radiation dropped off in $6 \mu\text{sec}$ when the laser was switched off (maximum possible time is $100 \mu\text{sec}$). Thus, the laser irradiation ceased practically instantaneously compared with the duration of the process forming an extended MR and, therefore, could be the reason for the appearance of the observed form of the termination of the region. The delay time of the formation of the edge of the extended MR from the formation of its central part is most likely associated with the thermophysical processes involved in the formation of such structures as well as with the mass transfer and distribution of the colloidal silver particles in the edge part of the region, requiring additional time.

Different variants of the butt-jointing of MR with one another were realized in writing extended MR in the interior of PCPG plates (Fig. 3). For example, Y-form MR (Fig. 3a) as well as MR intersecting at arbitrary angles (Fig. 3b) were formed. The maximum transverse diametric size of the cen-

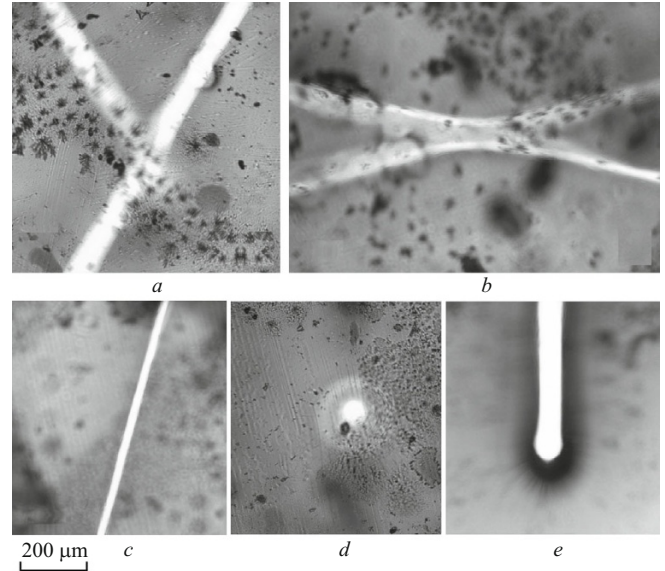


Fig. 3. Different implementations of MR written by a source moving in a transverse direction: Y- (a) and X-form (b), rectilinear MR with diameter $25 \mu\text{m}$ (c) as well as MR with diameter $50 \mu\text{m}$ written by a source moving in the longitudinal direction (d) and termination of MR in the interior (e). In all cases the optimal one-scan writing regime was chosen: $P_0 = 6.1$ W, $v = 18.5$ mm/sec. The photographs were made in transmitted light.

tral part for writing a good structure in one scan was $25 \mu\text{m}$ (Fig. 3c). The extended MR displayed in Fig. 3a–c were written with the source moving transversely relative to the optical axis of the laser beam. Another method of forming extended MR was writing with the source moving in a longitudinal direction, when the displacement of the beam waist started from the bottom surface of the PCPG and occurred along the optical axis of the laser beam in a direction toward the upper plane of the plate (Fig. 3d). This method made it possible to write MR with central part diameter equal to $50 \mu\text{m}$. In the course of the experiment the optimal laser processing regime for writing different regions in one scan was $P_0 = 6.1$ W and $v = 18.5$ mm/sec.

In the course of the experiments on butt-jointing of extended MR with different sizes it was determined that the jointing will be successful if the position of the beam waist when writing both structures will be located at the same distances from the surface of the plate. If this requirement is not satisfied, it is possible that the integrity of the edge parts of the butt-jointed waveguides in the region of intersection can be disrupted. When the sample was stopped and the laser radiation interrupted a spherical MR whose edge part was pulled in the direction of motion of the laser beam was formed in the interior of the PCPG plate (Fig. 3e). Beyond the limits of the optimal laser processing regime the size of an extended MR could be reduced, but in then its quality was degraded.

An important characteristic for the formation of MR is the volume energy density, which must be the minimum

amount required for structural changes in the region of the beam waist. No extended MR formed when the volume energy density dropped below the minimum value. A significant power reduction of the incident radiation and an increase in the number of scans with the minimum energy density in the beam being conserved likewise did not lead to the formation of extended MR. The modification process becomes accumulative, if an arbitrarily small change in the optical characteristics of the porous matrix of PCPG occurs in one scan. On this basis extended MR of smaller diameter were written with the lowest power of the incident radiation over several scans (Fig. 4). Y-shaped MR were recorded at $P_0 = 4.4$ W over three scans, and the sizes of the central parts were 14, 19 and 27 μm , respectively (Fig. 4a). It was also possible to obtain two single extended structures (Fig. 4b and c) with central-part diameters equal to 15–17 μm ($P_0 = 4.4$ W over three scans) as well as 7–9 μm ($P_0 = 3.5$ W over five scans). The scan rate was 18.5 $\mu\text{m}/\text{sec}$ in all three cases.

Spectral Characteristics of MR

The spectral curves of the transmission of PCPG plates and parts of extended MR before and after plates with MR were baked in a furnace are presented in Fig. 5. The minimum transmission in the range 475–525 nm of PCPG plates (2 in Fig. 5) indicates the presence of color centers in the plate, viz., particles of colloidal silver up to 60 nm in size, since the absorption band of the spherical silver particles lies in the range 480–500 nm [13, 14]. The transmission minimum near 500 nm attests to the presence of colloidal silver particles in the central part of MR (3 in Fig. 5). The higher value of the transmission coefficient in the central part of the region as compared with the values of these coefficients for a PCPG plate which has not been irradiated indicates a lower concentration of silver particles in the central part of extended MR. The spectral curve of the transmission of the edge part of the region (4 in Fig. 5), viz., the dark region surrounding the central part, is similar to a PCPG plate in terms the character of the change in the transmission curve but the transmission coefficient is lower in the entire experimental range of wavelengths. This indicates that the optical density in this region is higher than in a PCPG plate.

A characteristic of the transmission curves of a PCPG plate and the central part of an extended MR after baking is a very small increase in the coefficients of transmission in the entire range (5 and 6 in Fig. 5). Depending on the transmission of the edge part of MR after baking the increase in the transmission coefficients in the entire range is significant. This could be due to densification of the silica framework and distribution of the silver particles in the channels of the PCPG as a result of baking (7 in Fig. 5).

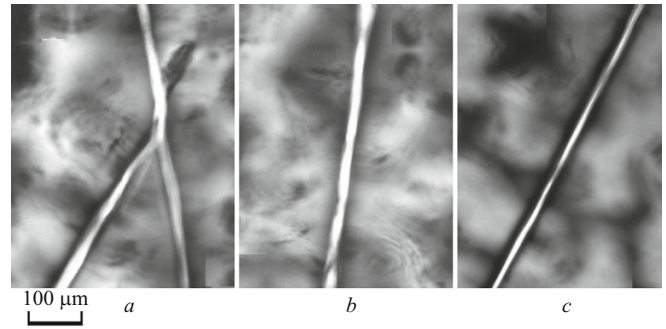


Fig. 4. Writing of MR over several scans with transverse movement of the source: a) Y-form; b) single MR ($P_0 = 4.4$ W, three scans); c) single MR ($P_0 = 3.5$ W, five scans). The photographs were made in transmitted light.

CONCLUSIONS

The results of investigations of the formation of extended MR in the interior of PCPG plates by means of laser radiation were described. The optimal irradiation characteristics required to write regions with minimum transverse size 25 μm in one scan and 8 μm in several scans were determined.

A complex structure of extended MR was found and the individual parts were studied by optical methods. In this case the spectral characteristics of the central and edge parts of MR were obtained.

It was demonstrated that it is possible to write MR with different configurations and forms comprising waveguide microstructures in the interior of glass which are fully capa-

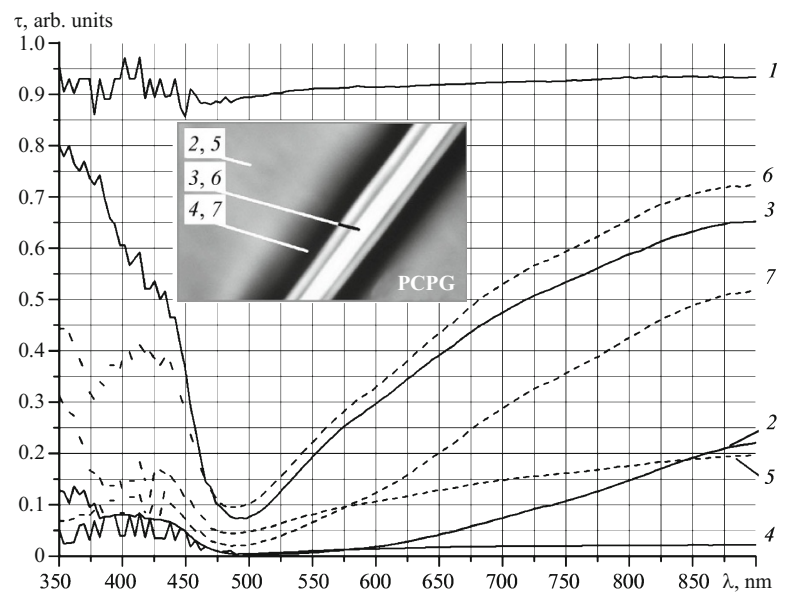


Fig. 5. Spectral curve of the transmission of a PCPG plate (2, 5) as well as the central (3, 6) and edge (4, 7) parts of the MR with respect to the transmission of a fused quartz plate (1) before (2–4) and after (5–7) a plate with MR is baked in a furnace.

ble of becoming the base elements of fiber-optic systems for different applications.

Financial support for this work was provided under the state financial support of the leading universities in the Russian Federation (subsidy 074-U01) and grant No. NSh 1364.2014.2 by the President of the Russian Federation for state support of the leading scientific schools in the Russian Federation.

REFERENCES

1. P. Predeep, *Optoelectronics: Devices and Applications*, InTech, Vienna (2011).
2. R. G. Jackson, *The Latest Sensors* [Russian translation], Tekhnosfera, Moscow (2007) (World of Electronics).
3. J. Gao, *Optoelectronic Integrated Circuit Design and Device Modeling*, Higher Education Press, Shanghai (2011).
4. A. I. Berezhnoi, *Sitals and Photositals* [in Russian], Mashinostroenie, Moscow (1966).
5. K. Sugioka, M. Meunier, and A. Pique, *Laser Precision Micro-fabrication*, Springer, New York (2010).
6. N. F. Borrelli, *Microoptics Technology*, Marcel Dekker, New York (2005).
7. G. K. Kostyuk, M. M. Sergeev, T. V. Antropova, et al., "Laser induced structural changes in porous glass due to hot and cold compaction," *Steklo Keram.*, No. 12, 1 – 5 (2013); G. K. Kostyuk, M. M. Sergeev, T. V. Antropova, et al., "Laser induced structural changes in porous glass due to hot and cold compaction," *Glass Ceram.*, **69**(3 – 4), 393 – 396 (2013).
8. I. K. Meshkovskii, *Composite Optical Materials based on Porous Matrices* [in Russian], Izd. SPbGITMO (TU), St. Petersburg (1998).
9. T. N. Vasilevskaya and T. V. Antropova, "Study of the structure of glassy nanoporous matrices by small-angle x-ray scattering," *Fiz. Tverd. Tela*, **51**(12), 2386 – 2393 (2009).
10. S. V. Stolyar, T. V. Antropova, D. V. Petrov, et al., "Viscosity and shrinkage of porous and quartzoid glasses obtained on the basis of the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$," *Zh. Prikl. Khim.*, **81**(6), 935 – 938 (2008).
11. V. A. Tsekhomskii, "Photochromic oxide glasses," *Fiz. Khim. Stekla*, **4**(1), 3 – 21 (1978).
12. M. A. Girsova, T. V. Antropova, I. A. Drozdova, et al., "Photochromic nanocomposites based on high-silica matrices from porous glasses," in: *3rd International Scientific Conference on Nanostructural Materials – 2012: Russia, Ukraine, Belarus NANO 2012* [in Russian], St. Petersburg, November 19 – 22, 2012, St. Petersburg (2012), p. 224.
13. A. A. Anikin, V. K. Malinovskii, and V. A. Tsekhomskii, "Spectral studies of silver-halide photochromic glasses," *Avtometriya*, No. 5, 65 – 71 (1978).
14. L. B. Glebov, N. V. Nikonov, and G. T. Petrovskii, "Writing information in photochromic planar waveguides on silicate glasses," *Avtometriya*, No. 5, 33 – 46 (1998).